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Integrity of clay till aquitards to DNAPL migration: Assessment using current and emerging characterization tools

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Abstract

Field investigations were carried out to determine the occurrence of tetrachloroethene (PCE) dense non-aqueous phase liquid (DNAPL), the source zone architecture and the aquitard integrity at a 30-50 year old DNAPL release site. The DNAPL source zone is located in the clay till unit overlying a limestone aquifer. The DNAPL source zone architecture was investigated through a multiple-lines-of-evidence approach using various characterization tools; the most favorable combination of tools for the DNAPL characterization was geophysical investigations, Membrane Interface Probe (MIP), core subsampling with quantification of chlorinated solvents, hydrophobic dye test with Sudan IV and Flexible Liner Underground Technologies (FLUTe) NAPL liners with activated carbon felt (FACT). While the occurrence of DNAPL was best determined by quantification of chlorinated solvents in soil samples supported by the hydrophobic dye tests (Sudan IV and NAPL FLUTe), the conceptual understanding of source zone architecture was greatly assisted by the indirect continuous characterization tools. Although mobile or high residual DNAPL (S_t >1%) only occurred in 11% of the source zone samples (intact cores), they comprised 86% of

the total PCE mass. The data set, and associated data analysis, supported vertical migration of DNAPL through fractures in the upper part of the clay till, horizontal migration along high permeability features around the redox boundary in the clay till, and to some extent vertical migration through the fractures in the reduced part of the clay till aquitard to the underlying limestone aquifer. The aquitard integrity to DNAPL migration was found to be compromised at a thickness of reduced clay till of less than 2 m.

Introduction

Dense non-aqueous phase liquids (DNAPLs) such as chlorinated solvents have been widely used and are common groundwater contaminants (Doherty, 2000; Mackay and Cherry, 1989). DNAPL release sites can have significant impacts on groundwater quality as the solubility of the chlorinated solvents may be several orders of magnitude above their regulatory limits. At DNAPL release sites where an aquifer is overlain by a clay aquitard, the groundwater quality in the aquifer will depend on the integrity of the clay aquitard as a barrier to the downwards migration of DNAPL. The low permeability clay aquitard will be associated with a high capillary resistance to DNAPL, which typically results in DNAPL pooling on top of the aquitard (Mercer & Cohen, 1990). Modelling of dual-porosity media has shown that further spreading of the contaminants may occur by transport of DNAPL in fractures, which are common in many aquitard systems, and in any coarser grained interbeds, and by the interrelated uptake of dissolved contaminants by matrix diffusion (e.g. Esposito & Thomson, 1999; Kueper & McWhorter, 1991; Parker et al. 1994, 1997; Reynolds & Kueper, 2001, 2004; Slough et al., 1999; VanderKwaak & Sudicky, 1996; Yang et al., 2012). Laboratory studies with both glaciolacustrine clay (O'Hara et al., 2000) and clay till (Jørgensen et al., 1998a) have shown that the fractures may act as rapid conduits for DNAPL migration in a manner that is difficult to predict. The integrity of the aquitard may therefore be compromised by extensive fracture systems. Observations of vertical fractures in Danish clay till show that fractures are common in the oxidized zone of the aquitard and that the likelihood of fracture development

53 throughout the entire clay till aquitard increases with decreasing thickness of the aquitard.
54 Furthermore, the thickness of a less fractured reduced zone and the drainage conditions below the
55 aquitard impact the extent of fractures (Klint et al., 2013). DNAPL migration in these fracture
56 systems will be affected by the matrix diffusion. The dual-porosity media can provide a
57 considerable retention capacity as the mass storage capacity of the matrix is generally much higher
58 than the storage capacity of the fractures (Parker et al., 1997). Hence, a significant volume of
59 DNAPL can be removed from the fractures through dissolution and subsequent diffusion to the
60 aquitard matrix, which may prevent migration of DNAPL through the fractured aquitard. The
61 specific entrapment and dissolution of DNAPLs will be very sensitive to heterogeneities in the
62 media (Poulsen and Kueper, 1992) including variations in the fracture aperture or even small-scale
63 variations in the individual fractures (Esposito & Thomson, 1999; Yang et al., 2012). Consequently,
64 thorough characterization of DNAPL source zone architecture is essential in relation to
65 management, risk assessment and remediation of sites with dual-porosity media.
66 The nature of the dual-porosity media, however, makes it difficult to locate the DNAPL and
67 determine the source zone DNAPL architecture. Parker et al. (2004) have made detailed field
68 investigations of the matrix diffusion of trichloroethene (TCE) into a glaciolacustrine clayey silt
69 aquitard with DNAPL pooled on top of the formation. Further studies can be aided by current and
70 emerging characterization tools for direct and indirect DNAPL detection such as: intact core
71 subsampling with depth-discrete VOC quantification (e.g. Griffin & Watson, 2002; Parker et al.,
72 2003; Rivett et al., 2014); hydrophobic dye test for direct visual confirmation of DNAPL through
73 dye partitioning into the DNAPL e.g. Sudan IV (Cohen et al., 1992; Griffin & Watson, 2002; Parker
74 et al., 2003; Rivett et al., 2014); FLUTe liners e.g. impregnated with a hydrophobic dye for visual
75 confirmation of DNAPL upon contact with the liner membrane (Broholm et al., 2016; Griffin &
76 Watson, 2002); Membrane Interface Probe (MIP) for continuous depth-discrete data obtained by
77 volatilization of contaminants, diffusion through the semi-permeable membrane and vapor detection
78 by e.g. Flame Ionization Detector (FID) (Adamson et al., 2014; Griffin & Watson, 2002; Rivett et

al., 2014); organic vapor analysis (OVA) screening of soil samples (headspace) or along intact cores with vapor detection by e.g. FID (Griffin & Watson, 2002); partitioning tracers (aqueous or gaseous) with an affinity to be detained in the DNAPL e.g. in the form of partitioning interwell tracer tests (PITT) (Hartog et al., 2010; Mariner et al., 1999) or soil gas surveys of natural occurring partitioning tracers such as radon, ^{222}Rn (Höhener & Surbeck, 2004; Schubert et al., 2007; Semprini et al., 2000); Laser-Induced Fluorescence (LIF) with continuous depth-discrete detection of emissions from DNAPL with inherent fluorescent properties e.g. aromatic compounds (D'Affonseca et al., 2008; Kram et al., 2001) or the modified Dye-Enhanced LIF (Dye-LIF) with injection of a hydrophobic dye and subsequent detection of fluorescent changes in the presence of DNAPL e.g. chlorinated solvents (Germain et al., 2014); and the Waterloo profiler with depth-discrete low-purge collection of groundwater samples (direct push) (Parker et al., 2003; Pitkin et al., 1999). Some of these characterization tools have previously been combined in a multiple-lines-of-evidence approach and compared for DNAPL characterization at sandy industrial sites (Griffin & Watson, 2002; Parker et al., 2003; Rivett et al., 2014). The use of these characterization tools at sites with strongly heterogeneous dual-porosity media is, so far, limited. When assessing the clay till aquitard integrity by a multiple-lines-of-evidence approach with the currently available characterization tools, near-continuous characterization tools are preferable as a high discretization is crucial in DNAPL characterization. The above characterization tools can also be supplemented with newer tools e.g. down-hole FLUTe liners with activated carbon felt (FACT).

The purpose of the investigations was to obtain a better conceptual understanding of the DNAPL source zone architecture (incl. chemical mass distribution) in fractured clay till aquitards, thereby improving the assessment of the integrity of the clay till aquitards in terms of aquifer protection and design of remedial actions at DNAPL release sites. The DNAPL source zone architecture was investigated by a combination of current and emerging site investigation methods for direct and indirect documentation of DNAPL, including most of the technologies mentioned above and the novel FLUTe Activated Carbon Technology. The characterization tools have mostly been applied to

aquifers and detailed studies on DNAPL migration in highly heterogeneous fractured clay tills aquitards are lacking.

Site description

The field site is a former distribution facility for tetrachloroethene (PCE) and TCE located at Naverland near Copenhagen, Denmark (Fig. 1). The facility was operational for 18 years (1965-1983) where an estimated 5000 tons of PCE (subsurface tank, 1.0-2.5 m below ground surface (bgs)) and 1700 tons of TCE (barrels) were handled. The distribution activities resulted in PCE and TCE DNAPL impacts to the fill and the fractured clay till (vadose zone) from surface spillage of the chlorinated solvents and/or subsurface leakage of PCE from the tank and/or the connection pipe to the southwestern end of the tank. The groundwater table is located approximately 6.5 m bgs, and the groundwater concentrations also indicate that the underlying fractured limestone aquifer (around 7-8 m bgs) may be impacted by DNAPL.

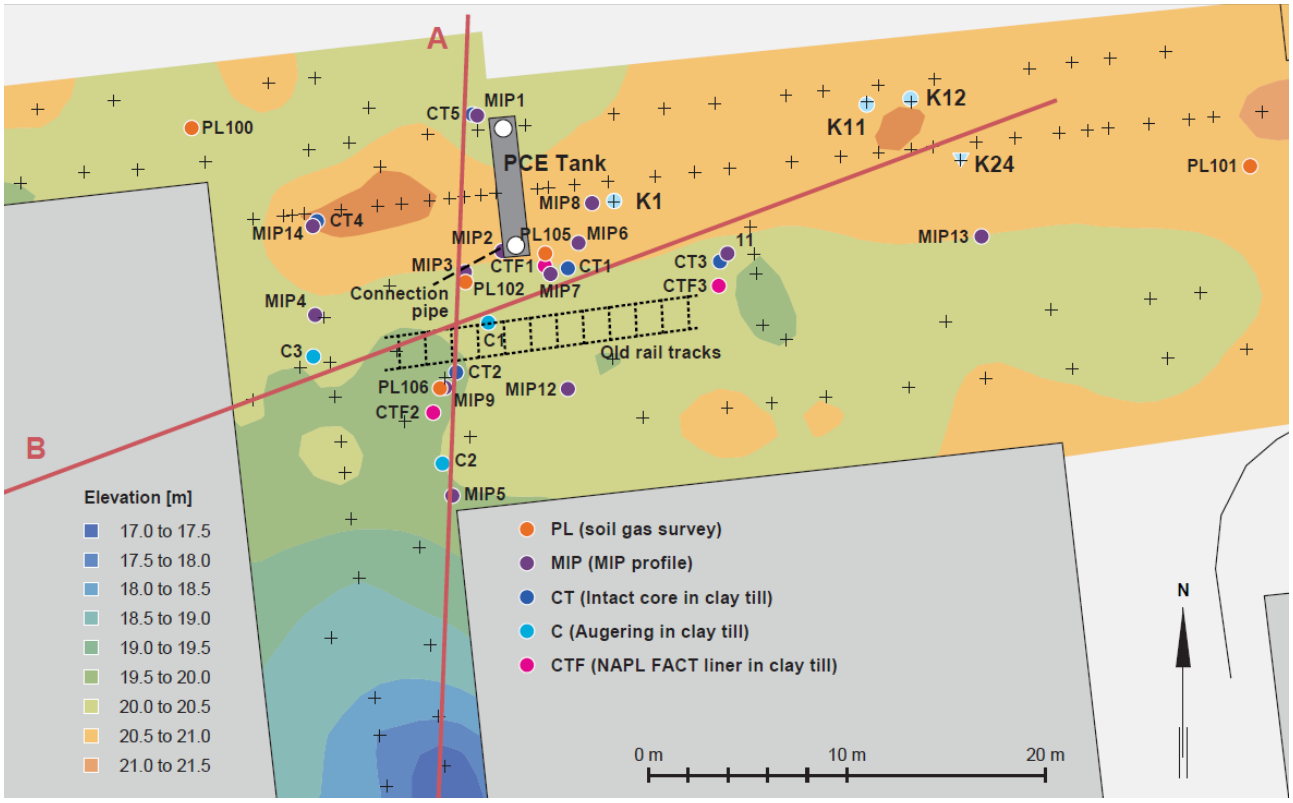

Fig. 1. Overview map of the site with structures (buildings, the previous PCE storage tank with connection pipe, and part of the old rail tracks, north of which the solvents were unloaded), the clay till surface elevation (m above sea level), the 13 MIP profiles (MIP1-9, MIP11-14), the five intact clay till cores (CT1-5), the three auger drillings (C1-3), the

three FACT NAPL FLUTe installations (CTF1-3), and the five soil gas surveys (PL100-102, PL105-106). The red lines indicate part of the geological cross-sections (A and B) in Fig. 2.

Materials and methods

Investigative approach

Characterization of DNAPL architecture is challenging, and to improve the robustness of the conceptual model, a multiple-lines-of-evidence approach was utilized to obtain data for the conceptual model. The more consistent the different lines of evidence are with a DNAPL architecture scenario, the more plausible the given scenario. The lines of evidence approach combined site history (locations with DNAPL handling and storage), geological characterization (surface geophysics; redox boundary; fracture orientation, inclination, spacing and aperture; and saturation conditions) and a number of direct and indirect characterization tools for detection of DNAPL (Table 1) with different spatial data resolution.

Table 1. Selected characterization methods for direct/indirect and continuous/point determination of DNAPL.

	Direct methods	Indirect method
Continuous	Flexible liners (NAPL FLUTe)	Membrane Interface Probe (Electron Capture
	Hydrophobic dye tests (Indigo Blue spray)	Detector (ECD), FID)
		Concentrations on activated carbon (FACT FLUTe)
Point	Hydrophobic dye tests (Sudan IV)	Partitioning tracer (natural radon)
	Direct observations of DNAPL (water or soil)	Organic vapor analysis (OVA) by Photo Ionization
		Detector (PID) (soil samples)
		Calculations based on water, soil and/or pore air
		concentrations

Based on the site history, initial geological characterization was done in a 110x70 m area (surface geophysics) and along two cross-sections (50-75 m) to assess locations of possible DNAPL pooling on top of the clay till and preferential flow paths. MIP and soil gas surveys were used to delineate the most contaminated part of the DNAPL source area, the locations of these investigations were based on the site history and the geological characterization. The investigations in this area were supplemented with augering and intact coring with discrete subsampling (concentrations in clay till,

144 OVA, hydrophobic dye test) along with installation of FLUTe liners (NAPL, FACT) for method
145 comparison. Since the characterization methods utilize adjacent boreholes (1±0.5 m spacing), the
146 results will be subject to natural variations in the DNAPL distribution, which is controlled by small-
147 scale features. An overview of the different sampling locations is given in Fig. 1.

148 **Geological characterization**

149 The transition between different geological layers is based on: surface geophysics, i.e. ground
150 penetrating radar (GPR) with a combination of 100 MHz and 250 MHz antennas and seismic
151 reflection and refraction (SRR) using a Geometrics Geode Ultra-Light Exploration Seismograph;
152 observations from augering and intact coring; electrical conductivity (EC) logging during the MIP
153 profiling; and geophysical borehole logging (mainly gamma) of six existing wells. The surface
154 geophysics were used to determine the transition between fill, clay till and limestone, while the
155 observations from coring and logging were also used to assess the transition between the different
156 clay till units. Furthermore, the coring and augering was used to determine the location of the redox
157 zone in the clay till based on a color shift from oxidized yellowish brown to reduced (olive) gray.

158 The geological characterization was not sufficient for a thorough investigation of fractures;
159 assumptions regarding fractures are, therefore, primarily based on the *a priori* knowledge of the
160 ground moraine deposits typical in the Copenhagen area gathered through excavations at similar
161 sites within the area (Christiansen et al., 2008; Jørgensen et al., 2003; Klint, 2001). Observations
162 made during clay till core characterization are generally consistent with the *a priori* knowledge.
163 Textural properties of clay till material at a nearby site (15-20 km) are given by Jørgensen et al.
164 (1998b, 2002).

165 **Membrane Interface Probe (MIP) profiling**

166 A MIP-6520 heated probe with removable membrane and dipole electrical conductivity array was
167 mounted on a 5400 Geoprobe (direct push drill rig) with a GH41 hydraulic hammer for probe rod
168 advancement. The probe was heated to 120°C and the diffused gasses were collected by nitrogen
169 carrier gas (40 mL/min) in a PTFE trunk line. The use of a halogen specific detector (ECD) was

combined with a detector for a broader range of organic compounds (FID). Near-continuous data were collected with a speed of 0.4-0.6 m/min; the data collection was only interrupted by subsampling of the carrier gas for analysis on a calibrated GC-MS (HP 6890). The sensitivity and carry-over was monitored by ongoing response tests (cf. SI for more details). The probe was also equipped with a sensor for continuous EC logging, where clay-rich units are represented by higher EC readings.

Soil gas survey of natural occurring partitioning tracer (Rn^{222})

The pore air was collected at 2-3 depths using a GeoProbe to place the probes. Back pressure, the PID value, CO_2, CH_4 and O_2 were monitored until the soil gas probe was purged (stabilization) (cf. SI for more details). The pore air was analyzed for chlorinated solvents (GC, HP 6890) and Rn^{222} (scintillation cells, duplicates). Due to analytical issues associated with the chlorinated solvents, the data are only used qualitative to indicate likely DNAPL presence in areas where DNAPL has been confirmed by other methods.

Sampling of the clay till units

Intact core collection and subsampling

The intact coring was done by the GeoProbe Dual-Tube system (1.5" ID) at five locations. The cores were retrieved in PVC liners (38 mm wide; 1.2 m long), which were sealed with PVC stoppers and adhesive tape. The samples were stored vertically (same orientation as in the subsurface) at 10°C until they were subsampled (within 4 days). The intact cores were initially split in half lengthwise and subsampled in a ventilation hood. One half was utilized for hydrophobic dye test (Indigo Blue), while the other half was subsampled for chlorinated solvents analysis (pentane extraction; 258 samples in total), hydrophobic dye test (Sudan IV; 56 samples in total) and OVA readings (PID; 64 samples in total). Subsampling of the cores was done by small core drills (0.5-1 cm ID) with a plunger. Subsamples were generally collected at high resolution around any observed larger fractures/lenses and/or at a set interval depending on the type of test. After the cores had been

subsampled for DNAPL characterization, a more meticulous geological assessment was performed for better insight into the small-scale geologic features of the source zone (cf. SI for more details).

Augering

Clay till samples were collected with a discretization of 0.5 m at depths between 1.0-8.0 m bgs at three additional locations (C1-C3) using augering equipment (the geology was documented during the field work). The clay till was sampled for chlorinated solvents analysis (pentane extraction), OVA screening (PID) and occasionally hydrophobic dye tests (Sudan IV). Additionally, certain clay till characteristics (porosity, bulk density, dry matter and water saturation) were determined based on six subsamples collected between 1.5-6.0 m bgs at C1.

Quantitative analysis

The clay till subsamples were extracted (using pentane) for analysis of chlorinated solvents. A known amount (by weight) of water (10 mL), clay till (5 g) and pentane (5 mL) were added to the extraction vial (40 mL VOA vial). The vial was vigorously shaken (vortex mixer) and placed in a rotation box at 10°C until the following day when the pentane was extracted and analyzed by GC-MS.

Organic vapor analysis

The organic vapor was analyzed using a Microtip 10.6 eV Krypton PID lamp calibrated with isobutylene gas. The cores were screened by running a handheld PID along the surface. Samples were collected and transferred to Rilsan® diffusion-proof bags, which were closed with headspace and stored at 4°C until the following day. Before the PID analysis of the headspace, the samples were acclimatized to room temperature (>4 hours).

Hydrophobic dye test

Two types of hydrophobic dye test kits from Cheiron Resources Ltd. were used i.e. OilScreenSoil® (Sudan IV) containing the hydrophobic red dye Sudan IV and a water soluble fluorescent green dye and OilScreenDNAPL-LENS Spray® containing the hydrophobic blue dye Indigo Blue (cf. SI for more details).

Flexible Liner Underground Technology (FLUTe)

The FLUTe is a tubular urethane coated nylon liner (Cherry et al., 2007). The liner was installed with GeoProbe (direct push) in three boreholes (CTF1-CTF3) as close as possible (approximately 1 m) to the intact cores collected at CT1-CT3. The inside-out flexible liner was attached to the casing (5.7 cm or 2.25") and pushed through the subsurface with the GeoProbe. The liner had a polyethylene pipe for air and/or water addition tethered inside the interior bottom of the liner. As the casing was withdrawn the liner was filled with air (0.7 bar) to push the liner against the borehole wall. Once the casing was removed the liner was filled with water (4.1 bar) to maintain the interior pressure against the borehole wall. Retraction was done by pulling the tether and inverting the liner. The liner was exposed to the borehole wall for 24 hours before retraction.

The liner was equipped with a NAPL FLUTe dye impregnated membrane. During the inside-out exposure of the liner in the borehole (24 hours) the membrane was in contact with the clay till formation. Any direct contact with NAPL in the formation should activate the dye and thereby form visible stains on the membrane. The liner was also equipped with a longitudinal strip of highly porous activated carbon felt, referred to as FACT. During exposure in the borehole, the FACT, contained within a diffusion barrier, was pushed against the clay till formation, which should result in sorption of the contaminant though contact with DNAPL, pore water and/or pore air. After retraction of the liner, the NAPL membrane was inspected on-site by cutting the inverted liner open; the locations of NAPL stains were documented. The FACT was cut in half lengthwise and subsampled in discrete subsections of 2-10 cm. The FACT subsamples were extracted (using pentane) for analysis of chlorinated solvents. A known amount (by weight) of water (10 mL), pentane (3 mL) and (by dimensions) FACT (0.06-0.32 g) were added to the extraction vials (20 mL VOA vials). At the end of the day, the vials were placed in a rotation box at 10°C for 84 hours before the pentane was extracted and analyzed on GC-MS.

GC-MS analysis

The pentane extracts from the clay till sampling and the FACT were analyzed by GC-MS using an Agilent 7980 gas chromatograph system equipped with an Agilent 5975C electron impact (70 eV) triple-axis mass-selective detector with a 30 m x 0.25 mm I.D x 1.40 µm film thickness ZB-624 capillary column (Phenomenex). Chloroform was used as the internal standard and detection and quantification limits were determined as described by Winslow et al. (2006) (cf. SI for details).

Data analysis

The DNAPL threshold concentration, C_T, of the chlorinated solvents in the clay till above which the presence of DNAPL would be suspected was calculated based on partitioning theory (Feenstra et al., 1991):

$$C_T = S \cdot x \frac{K_d \rho_b + n_w + n_a K_H}{\rho_b}, \quad (1)$$

where S is the solubility of the compound, x is the molar fraction of the compound, K_d is the partitioning coefficient between pore water and soil, ρ_b is the bulk density, n_w is the water-filled porosity, n_a is the air-filled porosity and K_H is the dimensionless Henry's law constant.

The DNAPL saturation can be given as the saturation of the total porosity, S_t:

$$S_t = (C_{Total} - C_T) \frac{\rho_b}{\rho_{DNAPL} n_t}, \quad (2)$$

where C_{Total} is the total amount of the chlorinated compound in the soil, n_t is the total porosity and ρ_{DNAPL} is the density of the DNAPL.

When considering the DNAPL saturation in a dual-porosity media, it can be relevant to distinguish between the total porosity and the fracture porosity. The fracture porosity, n_f, is given as (McKay et al., 1993):

$$n_f = 2 \frac{2b}{2B}, \quad (3)$$

where 2b is fracture aperture and 2B is fracture spacing.

Site specific values were obtained for the porosity (n_t, n_w, n_a), bulk density, ρ_b, and dry matter (samples from C1); the average values were n_t of 0.27 (σ = 0.01), n_w of 0.24, n_a of 0.03, ρ_b of 1.96 kg/L (σ = 0.03 kg/L) and dry matter of 91 % (σ = 2 %). The K_d values used for clay till were

determined at two similar clay till sites within 10 km of the Naverland site, and the values were 1.37 L/kg [0.84-2.45 kg/L] and 0.85 L/kg [0.62-0.96 kg/L] for PCE and TCE, respectively (Lu et al., 2011). The solvent densities used were 1.63 kg/L and 1.46 kg/L and the water solubilities were 0.00024 kg/L and 0.0014 kg/L for PCE and TCE, respectively (Broholm & Feenstra, 1995), while the dimensionless Henry's law constants used were 0.75 and 0.40, respectively (Pankow & Cherry, 1996).

Results and discussion

Site geology

The geophysics and the drilling/coring at the site showed an overall geology with a vadose zone consisting of a fill layer (0-1 m bgs) and two fractured clay till units (1-7 m bgs), an upper more fractured unit (ML1) and a lower sandier unit (ML2) (Fig. 2). The redox boundary was located around 5.0 m bgs (σ = 0.8 m) with a local depression in the area around CT2, C1 and C3. The EC logging confirms transitions around 2.8 m bgs (ML1 to ML2) and 4.5 m bgs (redox transition) (cf. SI, Fig. S1). The local fluctuations in the position of the redox boundary are likely linked to variations in the development of vertical fractures, whereby locally more developed fractures will result in a deeper lying redox boundary. According to Klint et al. (2013), Danish field observations show a medium to high likelihood of fractures throughout the clay till aquitard at sites where the thickness is less than 8-10 m (reduced clay till <3 m). This applies to the Naverland site, where the clay till layer is around 6 m thick (reduced layer of 1-3 m).

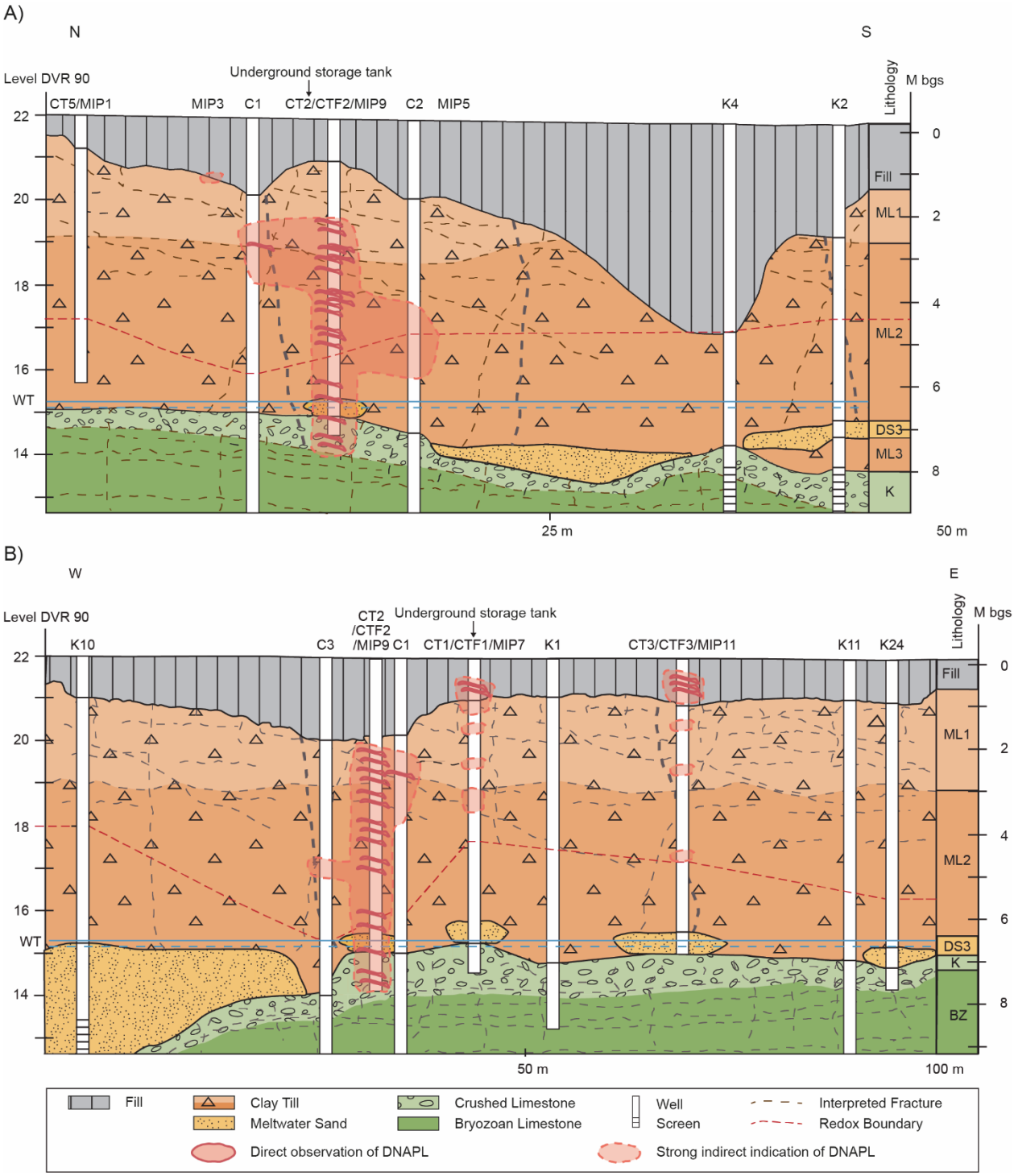

Fig. 2. Conceptual site geology (cf. cross-sections A and B on Fig. 1) with the approximate location of the redox boundary and direct observations and strong indirect indications of DNAPL. Fractures are interpreted fractures representing the higher frequency in the upper clay.

The inclination and orientation of the geological surfaces and fractures are of great importance for understanding the potential migration of DNAPL in the clay aquitard. The geophysics at the site showed that the surface of the clay till formation was generally dipping towards the S/SW (Fig. 1).

The glacial deposits in the area are associated with advances of Baltic ice from the southeast (Kjær et al., 2003). The fractures in the clay till generally originate as glacial-tectonic (sub-horizontal shear, conjugating sub-vertical shear and vertical extention) and contraction (freeze-thaw and desiccation) fractures. The vertical extension fractures are oriented in the direction of the ice movement (SE-NW), while the sub-vertical shear fractures are oriented perpendicularly to the ice movement (SW-NE). The shear fractures generally have an inclination dipping in the same direction as ice advancement (Klint, 2001), where the most developed fractures have an inclination dipping towards the SE, while a less developed fracture system has an inclination dipping towards the NW (ice recession and ice advancement, respectively).

The contraction fractures have a more irregular orientation and become less frequent with depth (Klint, 2001; McKay et al., 1993). The upper 3.5-5 m above the redox boundary are expected to be impacted by numerous contraction fractures. Observations showed an average fracture spacing of around 30 cm in the upper 3-4 m. Fracture spacing has been classified for 13 Danish clay sites (Jørgensen et al., 2003; Klint, 2001). The spacing above the redox boundary is generally 5-30 cm, while it gradually increases below the redox boundary with a spacing of 40-180 cm at 7 m bgs (Jørgensen et al., 2003). For Danish sites, clay till fracture apertures of 10-80 µm have been reported (Jørgensen et al., 1998b, 2002), which is similar to values reported for other clay tills (e.g. McKay et al., 1993). An average fracture aperture of 50 µm has been reported for clay till (Jørgensen et al., 2002; McKay et al., 1993).

Above the groundwater table, the clay till matrix is generally considered to be saturated, while the fracture systems are unsaturated. The water saturation is lower in the upper part of the clay till (67 % at 1.5 m bgs), and increases to 88 % (σ = 2.5 %) at 3.0-5.0 m bgs. The groundwater flow will predominantly be vertical through the larger fractures. The clay till is underlain by a thick bryozoan limestone aquifer, where the transition zone between the clay and the limestone consists of approximately 1 m of sand, gravel and brecciated limestone. According to Klint et al. (2013), the occurrence of fractures in the clay aquitard is increased if the underlying aquifer offers well-drained

conditions as the subglacial drainage conditions are a key factor for the deformation mode (ductile or brittle) of basal clay tills. The well-drained B-type basal till (brittle deformation) is more heterogeneous with systematic fractures. A highly transmissive aquifer, like the one at the Naverland site, will thereby increase the likelihood of fractures fully penetrating the clay till unit.

Based on the geology at the site, there is a relatively high risk that DNAPL could migrate though (sub-)vertical fractures in the clay till aquitard to the underlying limestone aquifer.

DNAPL migration

While the characterization tools can be used to assist in the horizontal delineation of the DNAPL source area (cf. Fig. 3), the main focus of the investigations was on the vertical migration of DNAPL within the source area for the assessment of the integrity of the fractured clay till aquitard. Most of the characterization tools were therefore focused on obtaining a vertical delineation of DNAPL. A comparison of methods for three points is presented in Fig. 4 and Fig. 5, while two additional locations are included in the SI (Fig. S2).

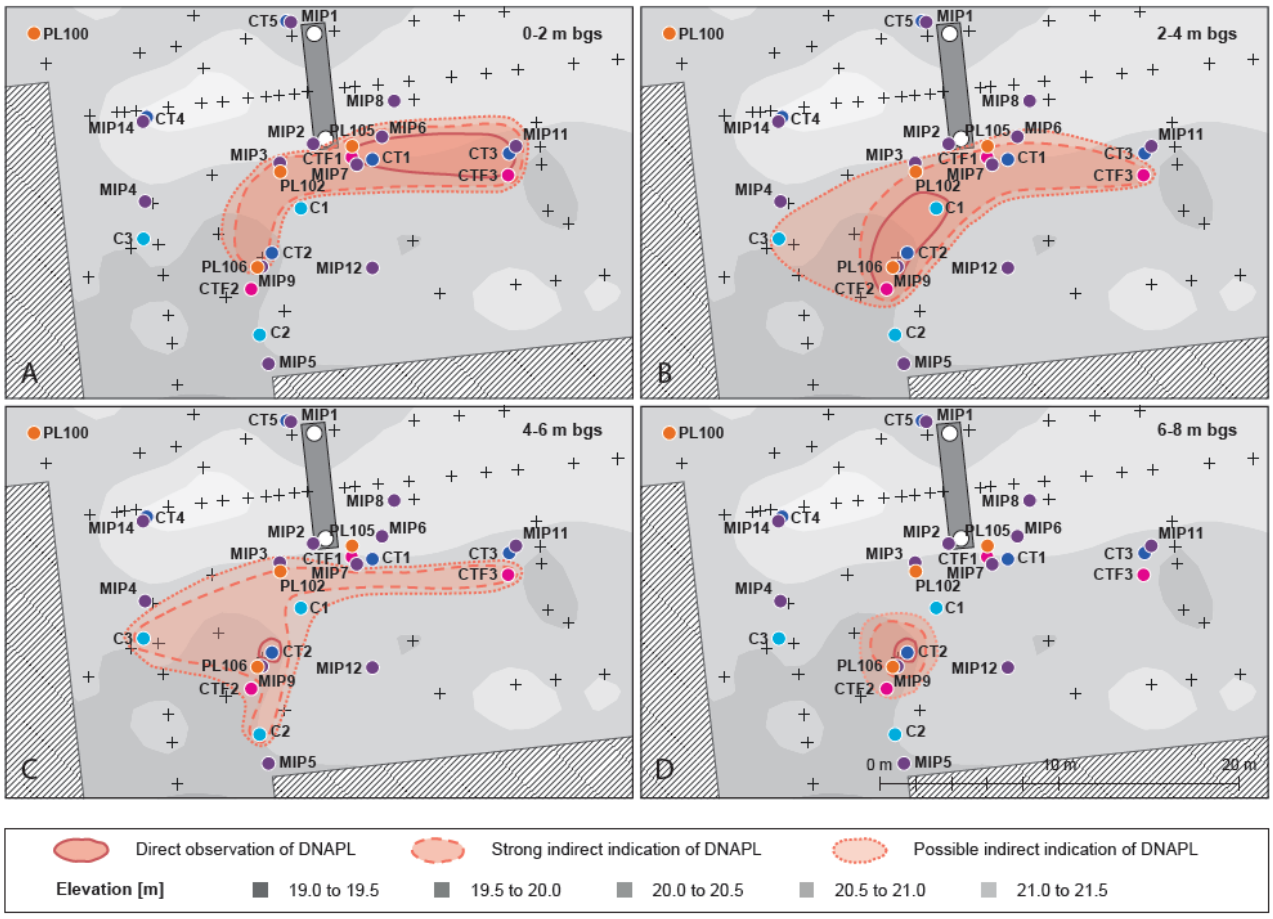

Fig. 3. Delineation of the horizontal DNAPL distribution in the source area in four depth intervals. The red lines indicate: direct observation of DNAPL by dye colorization test i.e. Sudan IV or NAPL FLUTe; strong indirect indication of DNAPL by contaminant concentration (S_T > 0 %), NAPL FLUTe smearing/spotting, high MIP response (FID ≥ 5 V), or high soil air concentrations (PID > 4000 ppm); and possible indirect indication of DNAPL by NAPL FLUTe transparency (increased transparency of line colors through the membrane), medium MIP response (2.5 V < FID < 5 V), or medium soil air concentrations (2000 ppm < PID < 4000 ppm).

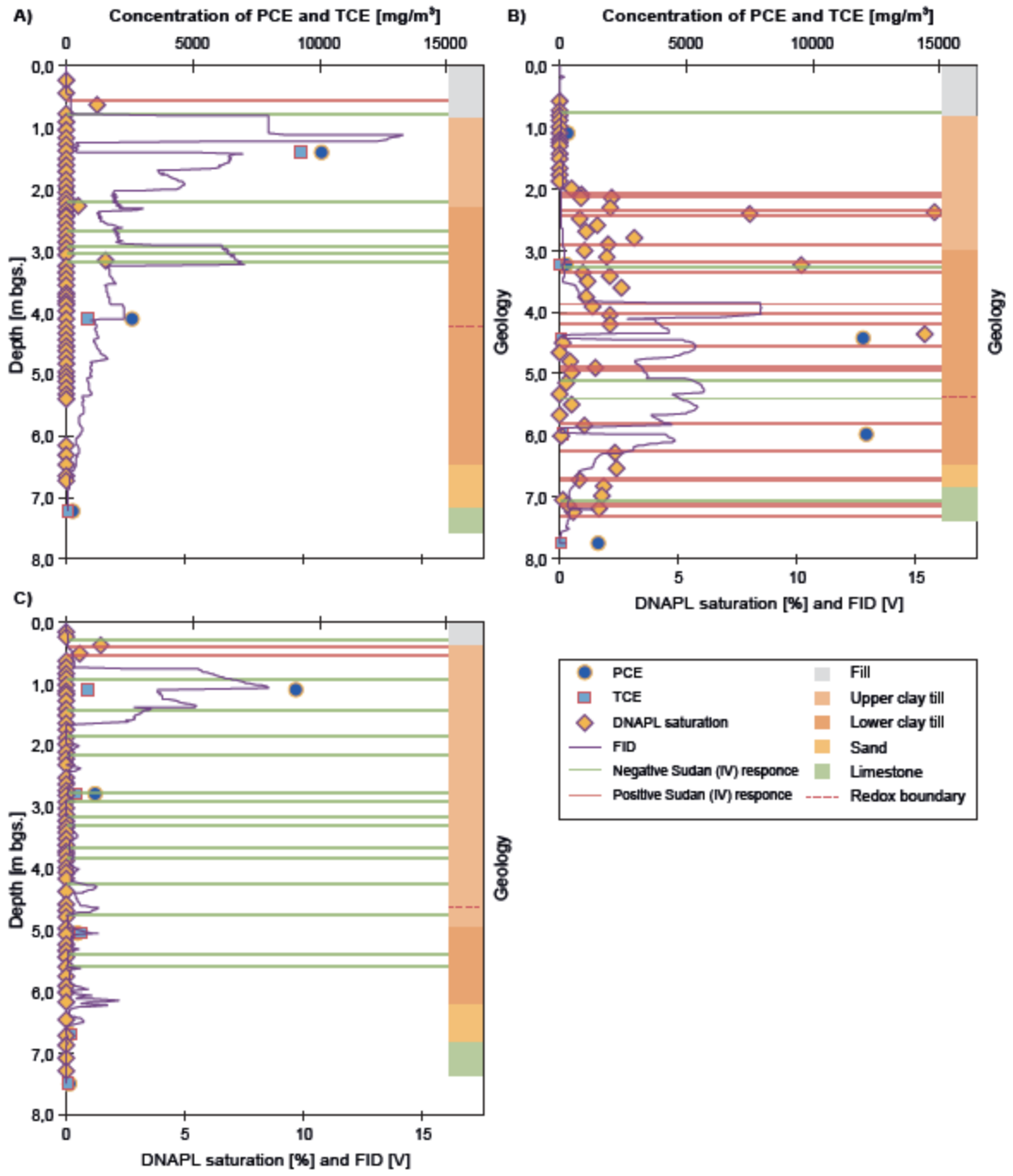

Fig. 4. Comparison of: DNAPL saturation (% of total porosity); PCE and TCE concentration (mg/m^3) in the carrier gas; MIP FID signal (V); and Sudan IV color response. a) CT1 + MIP7; b) CT2 + MIP9; and c) CT3 + MIP11.

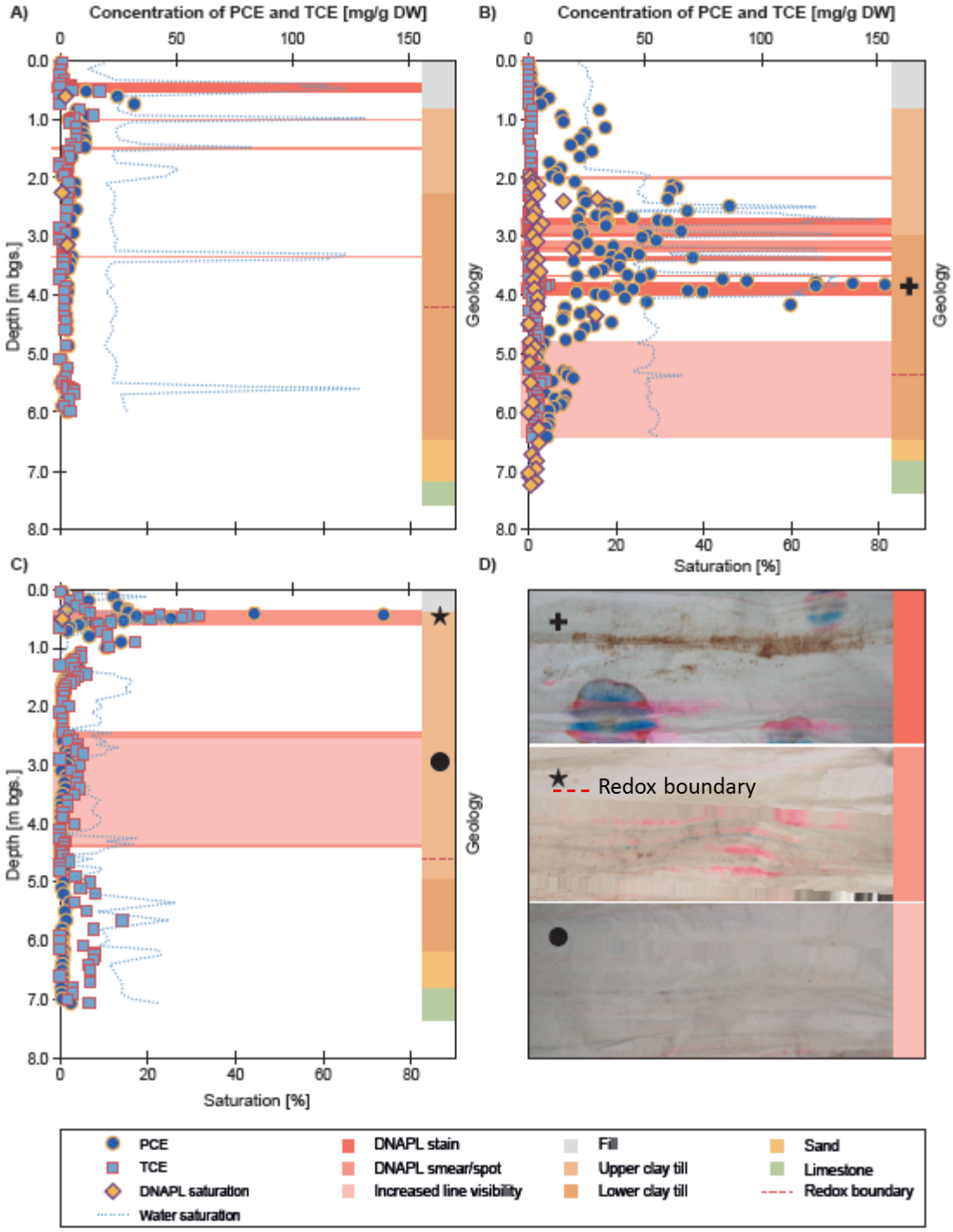

Fig. 5. DNAPL saturation (% of total porosity, only $S_t > 0$ % is included), water saturation (%) of the FACT material (not formation), PCE and TCE FACT concentration (mg/g DW) and NAPL FLUTE response comparison. The three pictures indicate the typical extent of staining (staining, smearing and transparency) on the FLUTe NAPL liner at the given color shade. a) CT1 + CTF1; b) CT2 + CTF2; c) CT3 + CTF3.

Clay till samples

The intact core recovery was generally good with an average recovery of 86 % (σ = 20 %). The average recovery was affected by a few unsuccessful core recoveries; while the majority of the cores had excellent recovery of more than 95 %. The discrete subsampling with quantification of chlorinated solvents was used as a reference for the other methods.

The main constituent of the DNAPL was PCE with an average TCE molar fraction of 0.031 (σ = 0.001). This is the case for the deeper laying DNAPL in the area southwest of the PCE tank (cf. Fig. 3), which likely originates from PCE leakage with TCE as an impurity. Locally, TCE molar fractions were higher (up to 0.49) close to the surface, especially in the area southeast of the PCE tank, where the DNAPL likely originates from spillage of solvents handled at the surface.

Based on the average DNAPL composition, the calculated DNAPL threshold concentrations (eq. 1) are 317 mg/kg for PCE [206-545 mg/kg] and 39 mg/kg for TCE [30-43 mg/kg]. The DNAPL threshold concentration is sensitive to sorption, the given concentration ranges indicate the possible variation in DNAPL threshold concentrations based on the variation found in K_d values for Danish clay till (Lu et al., 2011). The indicated variations in K_d values will have a limited effect on the calculated (eq. 2) DNAPL saturations (±0.2 %). The threshold concentrations are exceeded at three out of five intact core sampling locations (CT1-CT3) (Fig. 4).

The dye tests with Sudan IV for direct identification of DNAPL worked well for determination of PCE (or mixed PCE/TCE) DNAPL (Fig. 4). A color reaction was never observed in adjacent clay till samples containing PCE concentrations less than 250 mg/kg (below calculated DNAPL threshold), while concentrations of PCE in adjacent clay till samples above 1500 mg/kg (equal to 0.5 % DNAPL saturation of the total porosity) consistently resulted in coloration (cf. Fig. S4, SI). For the clay till samples with PCE concentrations in the in-between interval (250-1500 mg/kg), variable results were observed. This could be a result of false negatives due to interpretation issues with weak coloration or DNAPL dissolution at lower DNAPL saturations (<0.5 % of the total

382 porosity) and/or the variability in DNAPL saturation at even short distances, whereby the reference
383 concentration in the nearest clay till subsamples is not representative for the actual subsample used
384 for the dye test.
385 The blue-dye OilScreenDNAPL-LENS Spray® did not result in any visible coloration on the
386 grey/brown clay till cores. This was also the case for cores where DNAPL had been confirmed at
387 the opposite core half using the Sudan IV dye test. Hence, the spray was not a useful tool for
388 DNAPL determination at this clay till site.
389 The final measurement on the samples from the intact cores and the augering was OVA by PID
390 (cf. Fig. S3 in SI for maximum values). In previous studies with OVA by FID, readings exceeding
391 1000 ppm (Cohen et al., 1992) or 3000 ppm (Griffin & Watson, 2002) have been used to infer areas
392 associated with DNAPL (confirmed by other methods). When comparing the PID results of this
393 study with the calculated DNAPL threshold concentrations in samples from approximately the same
394 depth, the PCE concentrations were always above the threshold in the samples where PID > 4000
395 ppm. PID values > 4000 ppm were also correlated with 90 % of the Sudan IV tests that were
396 positive for DNAPL. The threshold was never exceeded when PID < 1000 ppm and all Sudan IV
397 tests were negative for DNAPL at PID < 1500 ppm (cf. Fig. S5-6, SI). For PID values between
398 1000-4000 ppm, indications of DNAPL varied; for PID < 3000 ppm only two indications of
399 DNAPL were found, while mixed indications were linked with PID of 3000-4000 ppm.
400 For two of the locations (CT1 and CT3), DNAPL was only directly observed (dye test) at the top
401 of the upper clay till unit with indirect indications of DNAPL in the oxidized clay till. For the third
402 location (CT2), DNAPL was directly observed (dye test) from 2 m bgs and throughout both clay till
403 units. CT2 is located in the area with a depression in the redox boundary; hence the presence of
404 DNAPL throughout the clay till units may be associated with locally more developed vertical
405 fractures in that area (cf. Site geology section). The DNAPL threshold concentrations were also
406 exceeded for the three less discretized augering locations C1-C3 (cf. Fig. 2), which are all located
407 close to CT2 (3-8 m), with DNAPL saturations of up to 4 % (direct observation of DNAPL by

Sudan IV), 2 % and 0.5 %, respectively. This is consistent with a deeper occurrence of DNAPL in the southwestern direction from the subsurface PCE tank (cf. Fig. 3). Hence, DNAPL spreading may occur in sub-vertical shear fractures with a NE-SW orientation (cf. Site geology section).

The data on the DNAPL threshold concentrations are summarized (Fig. 6) with regard to the frequency of occurrence and the mass distribution for each of the three intact coring locations with DNAPL (CT1-3) and for the total area (all five intact coring locations). The grouping of data is inspired by drainable core technique observations by Parker et al. (2003), where S_t < 10 % is linked with residual DNAPL (in a sandy aquifer) and on the grouping by Rivett et al. (2014) for a sandy aquifer (no DNAPL if $<C_T$; trace DNAPL if S_t <1 %; moderate residual DNAPL if S_t = 1-10 %; high residual DNAPL if S_t = 10-20 %; and pooled DNAPL if S_t > 20 %). The grouping has been modified to better suit a fractured media. Also, a lower uncertainty is involved with the trace DNAPL group. Hence the data is grouped in: no DNAPL ($<C_T$), trace DNAPL (S_t <0.2 %), moderate residual DNAPL (S_t = 0.2-1 %), high residual DNAPL (S_t = 1-2.5 %) and mobile DNAPL (S_t >2.5 %).

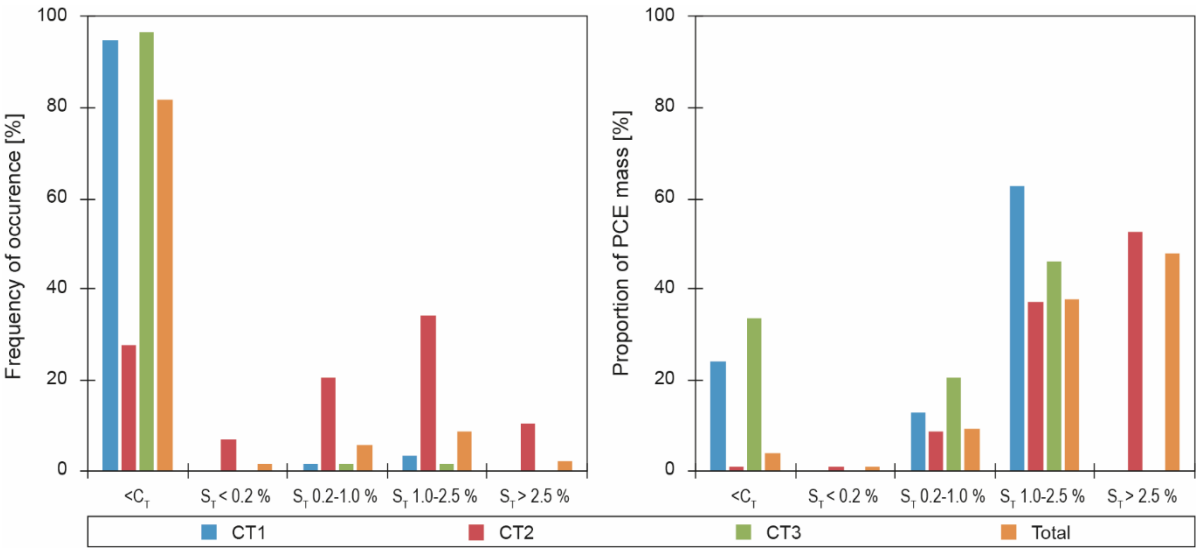

Fig. 6. Frequency of occurrence and the PCE mass distribution for each of the three locations with DNAPL above the threshold concentrations (CT1, CT2 and CT3) and for the total area (all five sampled locations). The data classification is inspired by the one used by Rivett et al. (2014). The classification is: No DNAPL (< C_T); trace DNAPL (S_t <0.2 %); moderate residual DNAPL (S_t = 0.2-1 %); high residual DNAPL (S_t = 1-2.5 %); and mobile DNAPL (S_t >2.5 %).

The trace DNAPL (<0.2 %) class is based on the uncertainty involved with the K_d values (±0.2 %). The residual DNAPL classes (moderate at 0.2-1 % and high at 1-2.5 %) are based on repeated observations of DNAPL throughout CT2 in this saturation interval (Fig. 4), while large NAPL FLUTe stains are found less frequent (Fig. 5) and therefore linked to mobile DNAPL at a higher saturation (>2.5 %). The divide between the moderate residual DNAPL (0.2-1 %) and high residual DNAPL (1-2.5 %) class is somewhat more arbitrary. In CT2 it was found, that the FLUTe transparency (5-6 m bgs) generally occurs at DNAPL saturations below 1 %, therefore the division at 1 %.

The occurrence of mobile DNAPL at significantly lower DNAPL saturations than in a granular media (Parker et al., 2003; Rivett et al., 2014) is ascribed to the fractures where the main DNAPL migration occurs in the dual-porosity media. Considering a realistic range of fracture apertures (10-80 µm) and fracture spacing (10-100 cm) the fracture porosity will constitute <0.01-0.60 % of the total porosity (eq. 3). This would indicate that the fractures are potentially completely saturated at most of the locations with DNAPL. However, since the subsamples, that the calculated DNAPL saturations are based on, represent small volumes, which were often collected at observed fractures, the fracture constitutes a larger part of the total porosity than it would on the overall field scale with larger fracture spacing; e.g. a 50 µm fracture would constitute 1.9 % of the total porosity in a 1 cm wide sample (n = 0.27) or 0.4-3.0 % for the 10-80 µm fracture range. This makes it reasonable to assume that mobile DNAPL could occur already at a DNAPL saturation of 2.5 % of the total porosity in the fractured media.

MIP

Due to high signal response for halogenated compounds, the ECD was unfortunately prone to overload (>845 V) and subsequent carry-over/drag-down at chlorinated solvent concentrations in the adjacent clay till samples far below (<10 %) the calculated DNAPL threshold concentration. Thereby the ECD was too sensitive to be used at the DNAPL source zone. This is consistent with

findings by Adamson et al. (2014), where overload and carry-over/drag-down for the ECD is observed at their “high concentration” area (<40 mg/kg CVOC).

Adamson et al. (2014) also used the less sensitive PID and FID for contaminant characterization in the saturated low permeable zones. However, the FID data were not evaluated beyond initial screening as the response was negligible. In the case of DNAPL, the low FID response to the chlorinated solvents can be a desirable trait making it more suitable as a characterization tool. In our case the FID response was significant, while not exceeding the measuring range (<15 V). The FID signal is not halogen specific and the relative response of PCE, TCE and DCE can be expected to be more or less the same with only very small differences due to the slight inhibitory effect on the response from the chlorine atoms (McDermott, 2004); however, the GC-MS subsamples (chlorinated ethenes, chlorinated ethanes and BTEX) confirmed that the response was mainly due to PCE and TCE.

For the locations without DNAPL (CT4-5) a reasonable linear correlation ($r^2 = 0.750$) was found between the sum of chlorinated solvent concentrations in the clay till samples and the average FID response in the adjacent sampling depths (cf. Fig. S7a, SI). These locations had a maximum concentration of chlorinated solvents (PCE and TCE) of 130 mg/kg and FID response of 1.2 V. For the locations with DNAPL (CT1-3), no linear correlation could be found ($r^2 < 0.01$) (cf. Fig. S7b, SI). This is not surprising as the most significant FID response peaks and the maximum chlorinated solvent concentrations in the adjacent cores are not exactly aligned, indicating a significant spatial variation even within relatively small distances (<1 m). Still, the overall trends from CT1-CT5 were captured reasonable well by the nearby MIP7, MIP9, MIP11, MIP14 and MIP1 (cf. Fig. 4 and Fig. S2 in SI).

While no direct correlation between FID responses and DNAPL saturation could be made, the MIP profiles (6, 7, 9, 11) representing the DNAPL source zone (DNAPL confirmed by dye tests in nearby cores) gave maximum FID responses between 4.8 V and 14.2 V, whereby FID responses above 5 V give a strong indication that DNAPL is present at the location. The MIP profiles outside

the DNAPL source area (no DNAPL confirmation or indication in nearby cores) had maximum FID responses of 2.1 V. It is therefore unlikely to find DNAPL if the FID response is consistently below 2.5 V given response tests of the same magnitude (15-75 mV response was observed for FID at 5 mg/L PCE solution).

Although no direct correlation was found, the MIP profiling showed significant variations in the FID response and was useful as a screening tool for both vertical and horizontal delineation of the DNAPL area in the low permeable clay till in the vadose zone. The findings were consistent with the historical knowledge on the site. Shallow contamination was found in the eastern part of the area (MIP11, 13) with surface handling of solvents and deeper contamination starting around the redox boundary in the western part of the area (MIP2, 4, 5, 9, 12, 14) where the geological characterization indicates DNAPL would migrate if leaked from the PCE tank. In the central part of the area (MIP3, 6, 7) a combination of the two contaminant profiles was observed.

NAPL FLUTe

A NAPL FLUTe was installed adjacent to each of the three boreholes (CT1-3) where the highest concentrations of chlorinated solvents were detected and the presence of DNAPL was confirmed by hydrophobic dye tests. In CT1 and CT3 direct evidence of DNAPL was found around 0.5 m bgs (cf. Fig. 4). The presence of DNAPL at this depth was confirmed by staining in CTF1, while a significant smearing of the colored lines was observed in CTF3 (cf. Fig. 5).

In CT2, direct evidence of DNAPL was repeatedly found at 2-7.5 m bgs (Fig. 4). At the depths with the highest DNAPL saturation (2-4 m bgs), staining was found in CTF2 (Fig. 5). At this depth interval, the average DNAPL saturation was 2.9 % of the total porosity, which indicates that mobile DNAPL is present in the fractures at this DNAPL saturation. Contact between the NAPL FLUTe and mobile DNAPL in hydraulically active horizontal fractures is thereby very likely at these depths. At greater depths, where the DNAPL saturation was below 2.5 % of the total porosity, the adjacent NAPL FLUTe liner showed slightly more visible colored lines, but no staining was

observed. The NAPL FLUTe thereby gives the impression that less DNAPL is present compared to the subsampling of cores at the adjacent location.

The NAPL FLUTe liner is a good tool for direct determination of DNAPL in the borehole. However, the presence of nearby DNAPL without direct contact to the borehole wall will not be detected. Concerns that the presence of residual DNAPL may be overlooked in the staining interpretation have previously been raised (Griffin & Watson, 2002). The nearby location of residual DNAPL may be indicated by the increased visibility of the colored lines. In initial laboratory studies (Beyer, 2012), it was found that high dissolved concentrations of chlorinated solvents would indeed increase the visibility of the colored lines. An aqueous solution saturated with both PCE and TCE would produce this effect, while a solution saturated only with PCE would not. Unfortunately, the effect will be difficult to interpret and does not give direct evidence of DNAPL.

FACT FLUTe

The FACT was employed to better delineate the concentrations over depth; direct contact with the DNAPL is not needed. The measured concentrations of PCE and TCE on the FACT are generally in good accordance with the observed staining/coloration trend on the NAPL FLUTe liner (cf. Fig. 5). In CTF1 and CTF3 the highest concentrations on the FACT are measured at 0.4-0.6 m bgs, where staining (CTF1) or smearing (CTF3) of the NAPL FLUTe liner is observed and DNAPL is directly observed in the adjacent core samples (cf. Fig. 4).

Interestingly, while DNAPL saturations (~1.5 %) in the adjacent core samples at a depth of around 0.5 m bgs are comparable for the two locations, the staining on the NAPL FLUTe and the PCE concentration on the FACT were very different (4 times higher in CTF3). The higher FACT concentrations in CTF3 are likely a result of the less saturated conditions; at 0.5 m bgs the FACT had water saturations of around 60 % and 30 % in CTF1 and CTF3, respectively. Preliminary laboratory results indicated more extensive sorption on the FACT in saturated air than saturated water (Beyer, 2012) as the diffusion coefficient of PCE in air is four orders of magnitude higher

than in water (Mendoza et al., 1996). Hence, the concentrations in the clay till and on the FACT cannot be directly correlated under variable saturation conditions (cf. Fig. S8).

Greatly elevated PCE concentrations were observed on the FACT in CTF2 at 2.0-4.5 m bgs, which correlates well with the depths where staining on the NAPL FLUTe liner was repeatedly observed (Fig. 5) and the depths were the DNAPL saturations in the adjacent core samples were high (Fig. 4). At greater depths (4.8-6.4 m bgs), somewhat elevated PCE concentrations were observed on the FACT, which correlates to the slightly more visible colored lines that were observed on the liner (Fig. 5) and DNAPL saturations in the adjacent core samples were in the residual groupings (Fig. 4). The TCE concentrations on the FACT in CTF2 were generally lower than in the two other liner boreholes, which is consistent with a lower molar fraction of TCE in the deeper contamination as observed in the intact coring.

The water saturation of the FACT varied significantly over depth and between the boreholes (Fig. 5). The average water saturation of the FACT in the three boreholes was 26 % (σ = 21 %), 37 % (σ = 19 %) and 10 % (σ = 7 %) for CTF1, CTF2 and CTF3 respectively. In comparison, the saturation of the less porous clay till formation was around 90 %, which correspond to a saturation of around 25 % given a porosity of 0.97 (FACT) instead of 0.27 (formation). In general, the water saturation of the FACT can be linked to observation of staining on the NAPL FLUTe and to some degree the DNAPL saturation in the adjacent cores. The linkage is most visible in CTF1, where the baseline water saturation on the FACT was around 13 % and six significant peaks of higher water saturation were observed. Four of the five largest peaks (>40 % saturation) correspond to the four observations of staining on the NAPL FLUTe, which may correlate to the presence of significant hydraulically active fractures where DNAPL can be transported. These peaks are also relatively well correlated to the depths with the highest FID responses in the adjacent MIP7. Very local occurrence of DNAPL in single fractures is in good accordance with the nature of DNAPL observations in the adjacent CT1 cores, where only one of the three single point observations of

555 chlorinated solvents above the DNAPL threshold concentration could be confirmed by adjacent
556 Sudan IV test (5-10 cm spacing).
557 In CTF2, the baseline water saturation is similar to CTF1 in the upper 2 m, but no peaks in water
558 saturation were observed; no staining on the NAPL FLUTe or DNAPL saturation in the adjacent
559 cores was observed in these upper 2 m. Deeper than 2 m bgs, the baseline water saturation on the
560 FACT is higher than in the other two locations (around 27 %), indicating a more water conducting
561 area. At depths below 2 m bgs, varying degrees of staining on the NAPL FLUTe and DNAPL
562 detection in the adjacent cores were observed. At 2.5-4.0 m bgs, several closely spaced peaks in the
563 water saturation (>60 %) were observed; those depths correlate well with the observation of
564 staining on the NAPL FLUTe and the highest DNAPL saturations (>3 %) in the adjacent cores.
565 This may indicate a locally more fractured area in the clay till with better possibility of DNAPL
566 migration. Below 4 m bgs, the lack of saturation peaks indicates a less fractured area without
567 horizontal DNAPL migration. The FACT concentrations were still somewhat elevated, while no
568 staining was observed on the NAPL FLUTe, with only a slightly increased visibility of the colored
569 lines. Around 4.5 m bgs, the DNAPL saturation in the adjacent cores became lower (<2.5 %),
570 whereby the FACT concentrations likely originated from dissolution of nearby residual DNAPL.
571 In CTF3 the water saturation was generally low without a stable baseline saturation; an increase in
572 the water saturation was observed around the redox boundary at 4-5 m bgs. The highest water
573 saturation (30 %) was found around 0.5 m bgs, which was also the location with most visible
574 staining on the NAPL FLUTe and the only observation of DNAPL in the adjacent cores. This may
575 indicate an area with relatively few fractures and a greater importance of pore air diffusion in the
576 matrix.
577 Although the method only adds qualitative data, the FACT has been valuable for improving the
578 conceptual understanding of DNAPL distribution and mobility in the clay till, which is important
579 for the aquitard integrity assessment. The trends in concentrations on the FACT are generally in
580 good overall accordance with the staining on the NAPL FLUTe liner and the DNAPL saturation in

581 the adjacent core samples. The variable saturation conditions are seen as a main challenge with
582 regard to linking the FACT concentrations to possible DNAPL presence. Modeling has recently
583 been used for improved interpretation of FACT concentrations under saturated aquifer conditions
584 (Broholm et al., 2016). For clay till aquitards with more uniform saturation conditions (i.e. below
585 the water table) it may also be possible to better correlate contaminant concentrations in the
586 formation and on the FACT.

587 *Soil gas survey of natural occurring partitioning tracer (Rn^{222})*

588 The soil gas survey (radon and chlorinated solvents) was challenged by the high back pressure in
589 the dense clay till deposits, whereby the attempted vertical delineation was not possible. The most
590 useful results were achieved from the shallow sampling points (<1.5 m bgs), where soil gases
591 accumulated in the fill below the asphalt capping and samples were retrieved relatively easy.

592 The results for the source area (PL102, PL105 and PL106) show high PID measurements (>5000
593 ppm) and relatively high concentrations of chlorinated solvents in the soil gases indicating the
594 presence of DNAPL (cf. Table 2). The relative soil gas concentration of TCE was especially high in
595 the eastern part the source area (PL105), which is consistent with surface spillage of chlorinated
596 solvents during handling in that area compared to subsurface leakage of PCE in the western part of
597 the source area. The results from outside the source area (PL100 and PL101) show relatively low
598 PID measurements (<100 ppm) and relatively low concentrations of chlorinated solvents in the soil
599 gases.

600

601 **Table 2.** Soil gas survey for chlorinated solvents and Rn^{222} in shallow sampling points (<1.5 m bgs).

Location	Depth (m bgs)	Back pressure (mbar)	PID (ppm)	PCE (mg/m^3)	TCE (mg/m^3)	cis-1,2-DCE (mg/m^3)	Rn^{222} (kBq/m^3)
PL100	1.3-1.5	500	61	260	30	0.49	130
PL101	0.3-1.5	350	2.5	38	0.88	0.45	17
PL102[1]	1.1-1.2	450	5600	830000	5100	8.6	90
PL105[2]	1.0-1.1	<50	7100	200000	25000	67	30
PL106[2]	0.9-1.0	100	>10000	1600000	6800	<0.01	220

The chlorinated solvent concentrations are only used qualitatively to indicate likely DNAPL presence in areas where DNAPL has been confirmed by other methods. [1]Strong indirect indication of DNAPL in the area. [2]Direct observation of DNAPL in area.

602

603 With the presence of DNAPL in the source area, the Rn^{222} measurements should be lowere
604 compared to the natural background concentrations by partitioning into the DNAPL. However, the
605 natural variation in Rn^{222} is high for the clay till (17-130 kBq/m^3), whereby the Rn^{222} concentrations
606 in the DNAPL source area (30-220 kBq/m^3) are not statistically lower than the background levels.
607 Based on the combination of poor sampling conditions for soil gas in the dense clay till deposits
608 and the apparent high natural variation in the Rn^{222} in the heterogeneous clay till deposits, the use of
609 Rn^{222} as a partitioning tracer is not recommended for assessment of DNAPL distribution in clay till.
610 *Method performance and recommendations*
611 Based on the performance of the characterization methods (Table 3), the following lines of
612 evidence approach is suggested to build conceptual understanding at a fractured clay till site. Initial
613 screening by MIP-FID (with GCMS) is done to assist delineation of the DNAPL area and to select
614 locations for in-depth characterization with intact coring and subsequent installation of NAPL
615 FLUTe (with FACT) in the same borehole. Core sub-sampling is done for quantification of
616 contaminant (and DNAPL saturation estimates) and direct evidence of DNAPL by Sudan IV
617 hydrophobic dye test (discretization based on PID screening and fracture locations). The NAPL
618 FLUTe is used for direct (continuous) evidence of DNAPL and FACT FLUTe sub-sampling for
619 water content (unsaturated zone) and relative vertical contaminant distribution.
620
621 **Table 3.** Performance of the characterization tools and recommendations for use at fractured clay till DNAPL sites.

Method		Performance	Recommendation
Intact cores: Concentrations/DNAPL saturation		Good performance. Good core recovery possible in clay till.	Recommended for quantification of the contaminants (with DNAPL threshold concentrations) and estimation of DNAPL saturation (dependent on the uncertainty of site specific parameters).
Hydrophobic dye test:	Sudan IV	Good performance. No false positive DNAPL responses below the DNAPL threshold concentration. Mixed results at DNAPL saturations of 0-0.5 %.	Recommended for direct (point) evidence of DNAPL in clay till. May overlook low residual DNAPL saturations (<0.5 %).
	Indigo Blue spray	Poor performance. No observed color response at locations with confirmed DNAPL.	Not recommended for direct evidence of DNAPL in clay till.
OVA by PID (soil samples)		Low-medium performance. No DNAPL indications at responses <1000 ppm, while strong DNAPL	Useful for screening of e.g. core samples for selection of locations for further discretization.

		indication at responses >4000 ppm.	
MIP:	ECD	Poor performance. Detector overloaded at concentrations below the DNAPL threshold concentration.	Not recommended for DNAPL sites.
	FID	Medium performance. No DNAPL indications at responses <2.5 V, while strong DNAPL indication at responses >5 V.	Robust against detector overload in DNAPL areas. Recommended as a continuous screening tool (combine with GCMS) to roughly delineate the DNAPL area.
FLUTe liners:	NAPL FLUTe	Good performance. Residual DNAPL can be overlooked.	Recommended for direct (continuous) evidence of especially mobile DNAPL in clay till.
	FACT FLUTe	Medium performance. Data are hard to interpret. Adds discrete water saturation data on FACT (especially useful in unsaturated media).	Recommended for building conceptual understanding. Currently not useful for DNAPL detection. Further development needed.
Partitioning tracer:	Natural Rn^{222}	Poor performance. No statistical difference for DNAPL presence. High variability in background concentrations and difficult sampling conditions (high back pressure)	Not suitable for clay till as the natural variation of Rn^{222} is too high in this geological media.

DNAPL source zone architecture and aquitard integrity

The data set generated supports a division of the source area into an eastern area with a shallower DNAPL contamination (PCE and TCE) likely resulting from spillage in connection with surface handling; and a southwestern area with a deeper DNAPL contamination (primarily PCE) likely resulting from subsurface leakage from the PCE tank and/or the connection pipe to the tank (cf. Fig. 3). Most of the characterization methods were suitable for determination of the approximate depth of the contamination. The direct observations of DNAPL presence could only be made by intact coring and NAPL FLUTe, while both MIP-FID with GCMS (for compounds determination) and FACT supported the intact coring in assessing whether the contamination was primarily PCE or a combination of both PCE and TCE.

The DNAPL source zone architecture in the eastern area is represented by DNAPL at the interface between the fill layer and clay till aquitard (direct observations) and likely vertical and horizontal migration in fractures and/or other high permeability features above the redox boundary in the clay till (mainly strong indirect indications). The indirect indications of DNAPL in the clay till are found as single observations of residual DNAPL saturations (< 2.5 %) with some spacing (~1 m) in the

intact coring and spotting on the NAPL FLUTe coinciding with high water saturation on the FACT (conductive fractures), indications which are likely linked to separate fractures (cf. Fig. 4-5). No indication of DNAPL was observed in the reduced clay till. In the southwestern area, the DNAPL source zone architecture is represented by deeper DNAPL starting around 2 m bgs (direct observations). DNAPL migration occurs vertically through fractures in the upper part of the clay till (direct observations), horizontal migration along fractures and/or other high permeability features above the redox boundary in the clay till (mainly indirect indications), and at one intact coring location continued vertical migration through fractures in the reduced clay till to the underlying aquifer (direct observations). The migration primarily occurs in the southwestern direction from the PCE tank, which is consistent with the fracture orientation typical for the area (cf. Site geology section).

Based on the results, it is expected that extensive vertical DNAPL migration will occur in the upper oxidized part of clay till aquitards, where (unsaturated) fractures are most abundant. Significant horizontal migration will also occur at depths with high densities of horizontal fractures connected to the vertical fractures (e.g. around or above the redox boundary). For the less fractured reduced part of clay till aquitards, the vertical (and horizontal) migration will be more limited and the aquitard integrity to DNAPL migration is largely linked with the thickness of this reduced zone of the clay till aquitards (cf. Fig S14, SI).

At the site, the one location where the aquitard integrity was observed to be compromised is in good agreement with the geological understanding of high risk areas for extensive fracture systems throughout the clay till unit. This area is represented by a depression in the redox boundary (cf. Fig. 2), identified by a bulk color change, which is often linked with locally more developed fracture systems, and the thickness of the reduced clay till is less than 2 m. Based on the FACT FLUTe water saturation in the compromised location, the clay till appears to be more water conducting (fractured) than the locations in the eastern part of the source area. The most extensive fracture system indications coincide with the location of mobile DNAPL saturations (> 2.5 % encountered at

2.5-4.5 m bgs) with residual DNAPL saturations (< 2.5 %) in the remaining depths. Hence, the majority of the DNAPL is accumulated in the more extensively fractured clay till above the redox boundary, while smaller amounts of DNAPL have been observed to penetrate vertically into the less fractured reduced clay till and to some extent into the underlying brecciated limestone.

The compromised aquitard integrity towards DNAPL is further supported by comparison of the estimated mass discharge of dissolved PCE (~2 kg/year) from the DNAPL source area (cf. SI) compared to the mass discharge to the on-going remedial pumping system (~100 kg/year) in the limestone aquifer at the site. This would indicate that significant amounts of DNAPL have been discharged to the limestone aquifer.

The geological understanding is important for conceptual development. The fractured clay till in the greater Copenhagen area is relatively well-characterized based on excavations in the area. In areas without prior characterization of fractures, local excavations or use of outcrops, gravel pits or similar in the area are highly recommended. For characterization of horizontal fractures (and redox boundary) intact cores are useful, while the FACT FLUTe may give an indication of water conductive fractures in the vadose zone.

Conclusions

The investigations of the PCE source zone showed that 82 % of the samples from the intact coring did not contain any DNAPL (PCE was below the threshold concentration); those samples only comprised 4 % of the total PCE mass. The majority of the PCE source zone mass was found as mobile DNAPL (St > 2.5 %) associated with fractures in the clay till (48 % mass, 2 % occurrence) or as high residual DNAPL (St = 1-2.5 %) in the clay till (38 % mass, 9 % occurrence). Hence, high resolution site characterization is needed for proper mass estimation and design of remedial actions in the fractured clay till.

No single technique was sufficient for characterization of the DNAPL source zone architecture. However, insight into the source zone architecture in the clay till aquitard was especially assisted by the use of MIP as a continuous qualitative initial screening tool combined with NAPL FACT

FLUTe and coring with quantitative subsample analysis for establishment of DNAPL threshold concentrations and Sudan IV colorization tests for positive confirmation of DNAPL presence. Surface geophysics with ground penetrating radar (GPR) and seismic reflection and refraction (SRR) combined with geologic information supplemented conceptual understanding of the transport and distribution of DNAPL in the fill and clayey till.

The data set generated from the combined use of the various characterization tools supports the hypothesis that DNAPL released at fractured clay till sites migrated vertically through fractures in the upper oxidized part of the clay till aquitard, horizontally along fractures and/or other high permeability features around the redox boundary, and to some extent vertically through the fractures in the reduced part of the clay till aquitard to the underlying aquifer.

The integrity of clay till aquitards to DNAPL migration is linked with the thickness of the less fractured reduced zone. The vertical migration of DNAPL through the reduced aquitard was only observed where the reduced clay till is less than 2 m thick, which is consistent with geological studies on high risk areas for fracture development throughout clay till aquitards. The findings on clay till aquitard integrity to DNAPL migration are likely transferable to similar primarily oxidized clay till aquitards of limited thickness.

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